Project Report #2

TESTING OF HOMES IN FLINT MICHIGAN TO ASSESS DISINFECTION BYPRODUCTS IN HOT AND COLD WATER

Report on Samples Collected May 31, 2016

University of Massachusetts, Amherst

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SECTION A: PROBLEM DEFINITION / BACKGROUND

The issue of lead contamination in the City of Flint (MI) has been well documented over the past year. The Flint MI Water Crisis (Apr 2014 – present) resulted from an ill-fated decision to switch from Detroit water with corrosion control, to Flint River water without corrosion control. This switch immediately led to violations for bacteria, then TTHMs, unprecedented corrosion of iron mains, main breaks, and elevated lead in water. Recent research demonstrated that incidence of elevated blood lead in Flint children increased in association with the switch in water sources. In response, during October 2015, the water source was shifted back to Detroit, and extra orthophosphate corrosion inhibitor was added in December. More recently, there have been questions raised about possible links between skin rashes and the quality of hot water in some Flint homes. ***A key question is: How does the DBP water quality in hot and cold water piping in Flint homes compare with DBP water quality observed in hot and cold water piping from homes elsewhere.***

SECTION B: PROJECT METHODS

In this project we analyzed paired hot and cold water samples from a group of Flint homes and from control locations not in Flint. In this current sampling campaign, the control location was in Grand Blanc, MI.

All water samples were collected in heavy-walled borosilicate glass bottles (500 mL and 1L total volume) with Teflon-lined septum caps. Several bottles were collected from each location as the various analytical methods require different preservatives. Samples for volatile compounds were collected headspace-free. When collecting hot water samples, we used "piston bottles" equipped with a sliding falcon tube for maintaining headspace-free conditions during cooling and thermal contraction.

This report pertains to the May 31, 2016 sampling event. All samples were placed on ice and transported by car to Amherst, MA for analysis.

Table 1 Summary of Analyses and Procedures

DBP Group[1]	Method#	Method Type	Instruments	Precision
THMs, HANs, HKs, CP	UMA01	LLE/GC/ECD	Agilent 6890 GC	Varies, but typically ± 10%
Iodo-THMs and other volatiles	UMA06	LLE/GC/ECD	Agilent 6890 GC	Varies, but typically ± 10%
Total Organic Chlorine (TOCl)	UMA03	Ads/Combustion /IC	Mitsubishi TOX-Metrohm IC	typically ± 15%
Total Organic Bromine (TOBr) & Iodine (TOI)	UMA18	Ads/Combustion /ICPMS	Euroglass TOX/ Varian Elan 9000 DRC ICP/MS	typically ± 15%
Haloacetic Acids	UMA02	LLC/deriv./GC/ECD	Agilent 6890 GC	Varies, but typically ± 15%
Haloacids	UMA10	Isotope dilution LC/MS/MS	Acquity/Quattro Premier triple quadrupole LC/MS	Varies, but typically ± 20%
Haloacetamides (HAMs)	UMA11	SPE/GC/MS/MS	Varian 2200 Ion Trap GC/MS	Varies, but typically ± 15%
N-Cl-HAMs	UMA13	SPE/LC/MS/MS	Acquity/Xevo G2-XS QTof	typically ± 20%
Oxyhalides	UMA21 UMA25	LC/MS/MS	Acquity/Quattro Premier triple quadrupole LC/MS	Varies, but typically ± 10%
Halobenzoquinones (HBQs)	UMA15	LC/MS/MS	Alliance/Quattro Micro triple quadrupole LC/MS	typically ± 15%
Aldehydes	UMA04	Deriv./LLE/GC/ECD	Agilent 6890 GC	typically ± 10%

[1] See discussion for a complete listing of compound abbreviations

SECTION B 1: SAMPLING PROCESS DESIGN

Samples for analysis were collected from Flint homes and those from one control community (Grand Blanc, MI). Sampling was done by the UMass team in accordance with our pre-established protocol. Both hot and cold taps were flushed until a stable temperature was reached. Measurement were made on-site at the time of collection for pH, temperature and chlorine residual. Bottles were sealed with the appropriate preservative immediately upon collection. Samples are then placed on ice and transported back to UMass by automobile.

SECTION B 2: SAMPLING METHODS

Samples were collected in borosilicate heavy-walled glass bottles supplied by UMass. These samples included both cold water samples and hot water samples. Preservation of samples was accomplished by mixing with pre-loaded preservative in accordance with the particular method. Because different methods require different methods of preservation, it was necessary to collect more than one bottle from each collection tap.

SECTION B 3: SAMPLE HANDLING AND CUSTODY

Sample identities were maintained by attaching permanently secured labels to individual sample bottles. A spreadsheet log was used to cross-reference each sample with its origin. Samples from Flint and an adjoining community were transported to UMass for analysis by the sampling team.

All samples were adequately labeled to reflect the site location and bottle number.

SECTION B 4: ANALYTICAL METHODS

Disinfection byproduct (DBP) concentrations were measured following widely accepted protocols (e.g., Standard Method; APHA, AWWA, WEF 2012) when they exist, or by methods tested and developed or adapted at UMass. A summary of analytical procedures that were used in this work is provided in Table 1.

Table 2. Summary of Analytical Methods

DBP Group	Method#	Method Type	Instruments	Precision	Special QC Considerations
THMs, HANs, HKs, CP	UMA01	LLE/GC/ECD	Agilent 6890 GC	Varies, but typically ± 10%	
Iodo-THMs and other volatiles	UMA06	LLE/GC/ECD	Agilent 6890 GC	Varies, but typically ± 10%	
Total Organic Chlorine (TOCl)	UMA03	Ads/Combustion /IC	Mitsubishi TOX-Metrohm IC	typically ± 15%	Column breakthrough criteria; IX rejection criteria
Total Organic Bromine (TOBr) & Iodine (TOI)	UMA18	Ads/Combustion /ICPMS	Euroglass TOX/ Varian Elan 9000 DRC ICP/MS	typically ± 15%	Column breakthrough criteria; IX rejection criteria
Haloacetic Acids	UMA02	LLC/deriv./GC/ECD	Agilent 6890 GC	Varies, but typically ± 15%	
Haloacids	UMA10	Isotope dilution LC/MS/MS	Acquity/Quattro Premier triple quadrupole LC/MS	Varies, but typically ± 20%	Isotope Dilution methodology
Haloacetamides (HAMs)	UMA11	SPE/GC/MS/MS	Varian 2200 Ion Trap GC/MS	Varies, but typically ± 15%	SPE recovery criteria
N-Cl-HAMs	UMA13	SPE/LC/MS/MS	Acquity/Xevo G2-XS QTof	typically ± 20%	requires synthesis of standards each day
Oxyhalides	UMA21	LC/MS/MS	Acquity/Quattro Premier triple quadrupole LC/MS	Varies, but typically ± 10%	
Halobenzoquinones (HBQs)	UMA15	LC/MS/MS	Alliance/Quattro Micro triple quadrupole LC/MS	typically ± 15%	
Aldehydes	UMA04	Deriv./LLE/GC/ECD	Agilent 6890 GC	typically ± 10%	Stereoisomer criteria

SECTION B 5: QUALITY CONTROL

The basic objective of our quality control measures is to ensure that all data are valid. This policy must be realized from sample collection to reporting of the final data. As such, we have defined protocols for all aspects of the project that will minimize human and instrumental error and identify problems as they arise. This policy is reflected in the detailed descriptions given in the sections below. More information may be found in the project QAPP.

All calibration and QC data will be reviewed by the PI or QC Manager. They will verify that all instrument systems are in control (i.e., they meet the acceptance criteria specified in Table 2 and the QAPP) and that QA objectives for accuracy and completeness have been met as specified in the QAPP. If any QC data are outside of the acceptance criteria, the PI or the QC Manager will investigate the cause of the discrepancy. If the discrepancy is due to an analytical problem, the sample will be re-analyzed and, if possible, another sample will be immediately collected, analyzed, and reported. In any event, the potentially spurious data will be flagged with a data qualifier and the QC problem will be explained in the project reports.

To maintain good quality control, checks will be incorporated into the sampling and analysis program. Quality control checks will be accomplished by ensuring that proper calibration, sampling, transporting, analytical, and documentation procedures are followed.

As summarized in Table 2, the laboratory routinely analyzes the following quality control samples, depending upon the type of sample and the required analysis. Note that additional elements of QC are noted in the various SOPs. Detailed procedures can be found in the SOPs attached in the Appendix to the project QAPP

Internal Standards. A reagent that is available in high purity, stable, yields good detection, and does not react with the components of the sample is spiked into the sample as an internal standard. The internal standard will be soluble in the sample. These standards are used to monitor degree of sample pre-concentration, injection volumes as well as instrument performance and sensitivity.

QC Check Sample. A QC check sample is obtained by adding a predetermined amount of selected constituents into the reagent water. QC check samples are typically used at a rate of 1 out of every 10 samples. If a concentration value for a QC check sample is less than 85% or more than 115% of its predetermined value, the sampling and analysis procedure will be re-examined for sample matrix interferences, and errors in sample handling and/or analysis.

Calibration Standards. Standards of known purity are analyzed daily to calibrate instrument response and method response factors.

SECTION C: RESULTS AND DISCUSSION

In accordance with the request of the sponsor and the project QAPP, we are submitting reports on each of the sampling campaigns. This document is one of those reports focused on the second sampling event (May 31, 2016). Result from this event are compiled in the Tables 3 and 4 below. Locations A and C were nearby controls served by another system[2], whereas locations B and D were from Flint residences served by the Flint system.

Table 3. On-site Sample Analysis

Parameter	A		B		C		D	
	cold	hot	cold	hot	cold	hot	cold	hot
Temperature (°C)	17.1	43.2	16.1	50.1	18.0	42.7	18.9	42.4
pH	7.30	7.40	7.50	7.38	7.78	8.20	7.14	7.35
Chlorine Residual (mg/L)	0.52	0.05	0.18	0.03	0.14	0.02	0.77	0.57

[2] From locations in Grand Blanc or adjacent to Grand Blanc, information on service areas comes from Dr. Marc Edwards

Table 4a. Concentrations of DBPs found in May 31, 2016 Samples (all values are in µg/L)[3]

		Location A		Location B		Location C		Location D	
	Analyte	cold	hot	cold	hot	cold	hot	cold	hot
Oxyhalides									
	Bromate	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Iodate	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Trihalomethanes									
	CHCl3	35.8	44.7	36.3	35.1	47.5	49.7	31.2	45.5
	CHCl2Br	11.8	12.5	12.5	12.4	13.9	12.7	11.5	13.7
	CHClBr2	3.8	4.2	3.9	4.1	5.1	4.4	3.7	4.1
	CHBr3	0.2	0.2	0.2	0.2	0.5	0.3	0.2	0.2
	THM4	51.5	61.6	52.9	51.8	67.0	67.2	46.7	63.5
Halonitriles									
	TCAN	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	DCAN (ug/L)	0.87	1.37	0.99	0.58	0.30	0.04	0.89	2.08
	BCAN (ug/L)	0.54	0.60	0.54	0.20	0.27	0	0.54	0.83
	DBAN	0.15	0.16	0.13	0.06	0.12	0.00	0.15	0.19
	DHAN	1.56	2.13	1.66	0.84	0.69	0.04	1.58	3.09
Haloketones									
	1,1-DCP	0.17	0.93	0.15	0.47	0.06	BDL	0.11	0.72
	1,1,1-TCP	BDL	BDL	0.04	BDL	BDL	BDL	0.06	2.28
	HK	0.17	0.93	0.19	0.47	0.06	BDL	0.17	3.00
Halonitromethanes									
	CP	0.16	0.47	0.14	0.21	0.15	BDL	0.11	0.31
Halobenzoquinones									
	DCBQ	0.022	BDL	0.006	BDL	BDL	BDL	0.043	BDL
	DBBQ	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	OH-DCBQ	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Haloacetamides									
	MCAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	MBAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	DCAM	5.66	5.39	4.33	6.08	3.62	4.23	5.98	5.73
	BCAM	0.37	0.17	0.13	0.16	BDL	BDL	0.32	0.27
	TCAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	DBAM	0.14	BDL	0.09	BDL	BDL	BDL	BDL	BDL
	BDCAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	DBCAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	TBAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

[3] BDL = below detection limit; lost = sample lost or otherwise compromised, NM= not measured.

Table 4b. Concentrations of DBPs found in May 31, 2016 Samples (all values are in µg/L)

		Location A		Location B		Location C		Location D	
	Analyte	cold	hot	cold	hot	cold	hot	cold	hot
N-chloro-haloacetamides									
	N-Cl-DCAM	6.33	BDL	5.72	5.62	7.95	7.06	6.73	6.77
	N-Cl-BCAM	1.87	2.79	1.94	1.53	2.21	0.69	1.23	2.59
	N-Cl-DBAM	0.23	0.46	0.52	0.28	0.77	0.28	0.33	0.46
	N-Cl-TCAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	N-Cl-BDCAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	N-Cl-DBCAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	N-Cl-TBAM	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Haloacetic acids									
	MCAA	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	MBAA	0.46	0.40	0.20	0.38	0.48	0.45	0.43	0.45
	DCAA	9.44	5.08	8.36	6.31	15.15	8.20	14.82	14.41
	BCAA	3.52	2.35	2.05	2.28	4.37	3.07	4.01	3.94
	TCAA	6.89	6.98	5.85	6.67	5.48	6.21	5.43	5.45
	DBAA	0.58	0.35	0.37	0.48	0.98	0.68	0.84	0.84
	BDCAA	2.44	2.94	1.48	2.83	1.44	2.69	0.91	0.97
	CDBAA	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	TBAA	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	DHAA	13.54	7.78	10.77	9.07	20.49	11.94	19.66	19.19
	THAA	9.34	9.92	7.33	9.49	6.92	8.90	6.34	6.42
	HAA5	17.38	12.81	14.77	13.83	22.09	15.54	21.51	21.15
	HAA9	23.34	18.09	18.30	18.94	27.89	21.30	26.43	26.05
Iodo-THMs									
	CHCl2I	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	CHClBrI	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	CHBr2I	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	CHClI2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	CHBrI2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	CHI3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Aldehydes									
	Formaldehyde	2.1	6.0	1.5	4.4	BDL	0.6	0.3	2.3
	Acetaldehyde	NM	NM	NM	NM	NM	NM	NM	NM
	Propanal	1.4	1.8	1.3	1.5	1.2	1.6	1.2	1.4
	Butanal	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Pentanal	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Hexanal	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Heptanal	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Octanal	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Nonanal	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Decanal	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Glyoxal	2.0	3.4	1.1	1.6	1.0	0.5	1.0	2.0
	Methylglyoxal	BDL	3.1	0.2	2.6	0.7	0.2	BDL	0.6

Table 5a. Percent Increase in Concentrations of DBPs in Hot Water Compared to Cold Water from the same Residence (May 31, 2016 Samples)

		% Increase due to water heater			
	Analyte	A	B	C	D
Trihalomethanes					
	CHCl3	25%	-3%	5%	46%
	CHCl2Br	6%	-1%	-9%	19%
	CHClBr2	11%	6%	-12%	8%
	THM4	20%	-2%	0%	36%
Halonitriles					
	DCAN	57%	-41%	-86%	132%
	BCAN	11%	-63%	-100%	53%
	DBAN	8%	-56%	-100%	28%
	DHAN	37%	-49%	-94%	95%
Haloketones					
	1,1-DCP	453%	216%		531%
	1,1,1-TCP				Large Incr.
	HK	453%	143%		Large Incr.
Halonitromethanes					
	CP	201%	52%		170%
Halobenzoquinones					
	DCBQ	-100%	-100%		-100%
Haloacetamides					
	BCAM	-5%	40%	17%	-4%
	TCAM	-52%	26%		-16%

Table 5b. Percent Increase in Concentrations of DBPs in Hot Water Compared to Cold Water from the same Residence (May 31, 2016 Samples)

		% Increase due to water heater			
	Analyte	A	B	C	D
N-chloro-haloacetamides					
	N-Cl-DCAM		-2%	-11%	1%
	N-Cl-BCAM	49%	-21%	-69%	111%
	N-Cl-DBAM	103%	-46%	-63%	37%
	N-Cl-TCAM				
	N-Cl-BDCAM				
	N-Cl-DBCAM				
	N-Cl-TBAM				
Haloacetic acids					
	MBAA	-14%	91%	-5%	4%
	DCAA	-46%	-24%	-46%	-3%
	BCAA	-33%	11%	-30%	-2%
	TCAA	1%	14%	13%	0%
	DBAA	-40%	30%	-31%	0%
	BDCAA	20%	91%	87%	7%
	DHAA	-43%	-16%	-42%	-2%
	THAA	6%	30%	29%	1%
	HAA5	-26%	-6%	-30%	-2%
	HAA9	-22%	3%	-24%	-1%
Aldehydes					
	Formaldehyde	187%	199%	Large Incr.	713%
	Propanal	34%	23%	40%	10%
	Glyoxal	66%	42%	-54%	103%
	Methylglyoxal	Large Incr.	Large Incr.	-66%	

Trihalomethanes (THMs)

The average cold water TTHM value from the two Flint homes was 50 µg/L, whereas the Grand Blanc locations were at about 59 µg/L. This is higher than the last sampling event but not unexpected based on the higher system temperatures. It is also within 25% of the long-term seasonal trend observed for Flint (Figure 1). The bromine incorporation ratio for the Flint samples is 0.37 which is typical of a water with moderate bromide levels.

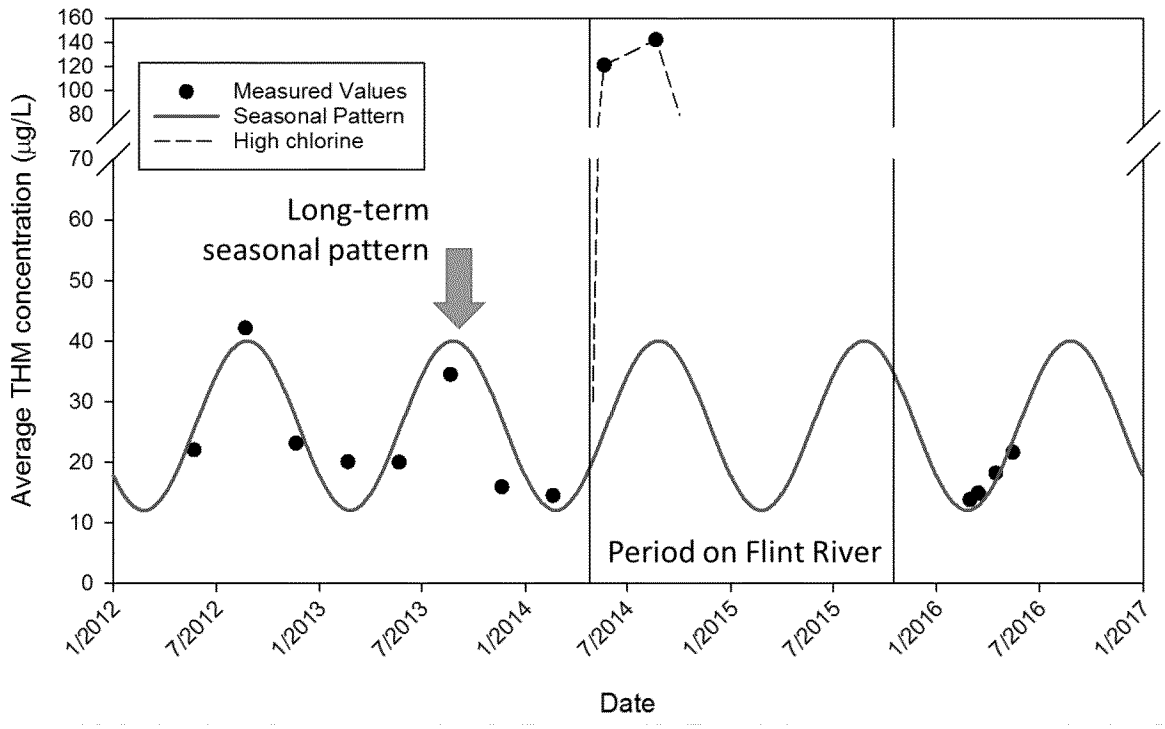

Figure 1. Long Term Trend for Average TTHM Concentrations in the Flint Distribution System

This observed concentration range of TTHMs collected from cold water taps in Flint corresponds to the 75-85 %ile nationwide (Figure 2). Given the warm weather period for this sampling event, higher than average THMs is not unexpected. Samples collected from hot water taps in Flint homes showed higher levels of THMs in one case and no change in the other. This pattern was repeated in the control community. Past experience suggests that the extent of change for THMs during premise heating is strongly linked to the loss of residual chlorine (Figure 3), which is often close to or the same as the residual chlorine in the cold water entering the water heater (i.e., loss of chlorine in water heaters is usually 80% or greater). Unlike the May 5th sampling event, we were able to measure both chlorine residual and temperature from all taps in the May 31st event. Our testing showed that the hot-water chlorine residuals had dropped to essentially zero in three of the four locations. In two of these locations (B and C) the chlorine residual in the cold water was also largely depleted, and for that reason, the increase in THMs due to heating was quite small. The other two (A and D) showed higher cold-water chlorine residuals (0.52-0.77 mg/L), with substantial chlorine depletion in the hot water plumbing (0.20 to 0.47 mg/L). As a result these two locations exhibited TTHM increases of 20% and 36%. Both are within the range observed in other US municipal systems (Figure 4).

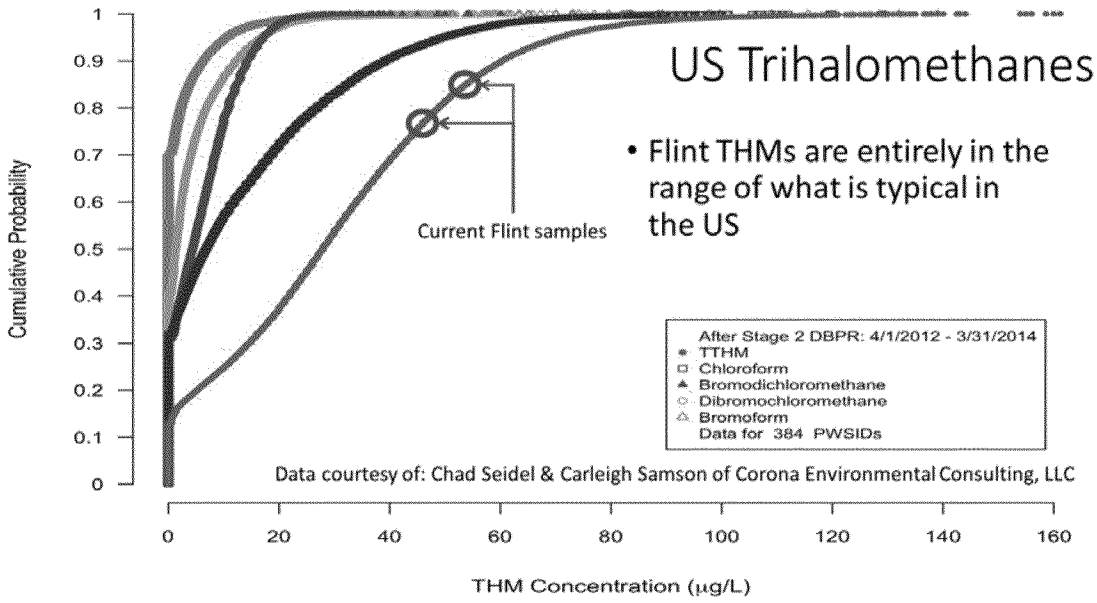

Figure 2. Comparison of Flint Distribution System THMs with National Database Prepared by Seidel and Samson.

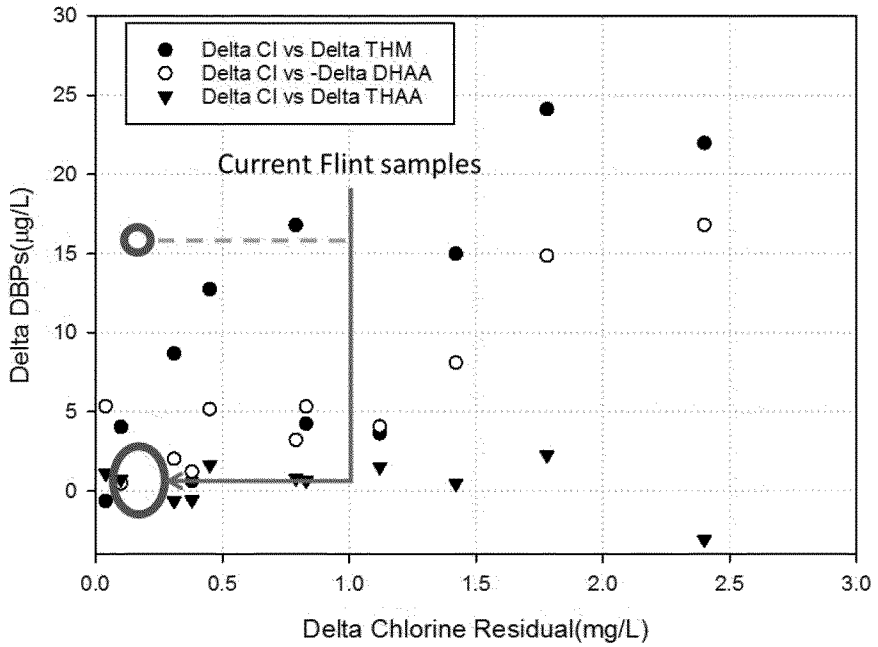

Figure 3. Effect of Chlorine Residual on Changes in THM and HAA Concentrations between Hot and Cold water for US Homes with Tank Heaters from one City (Reckhow, unpublished database)

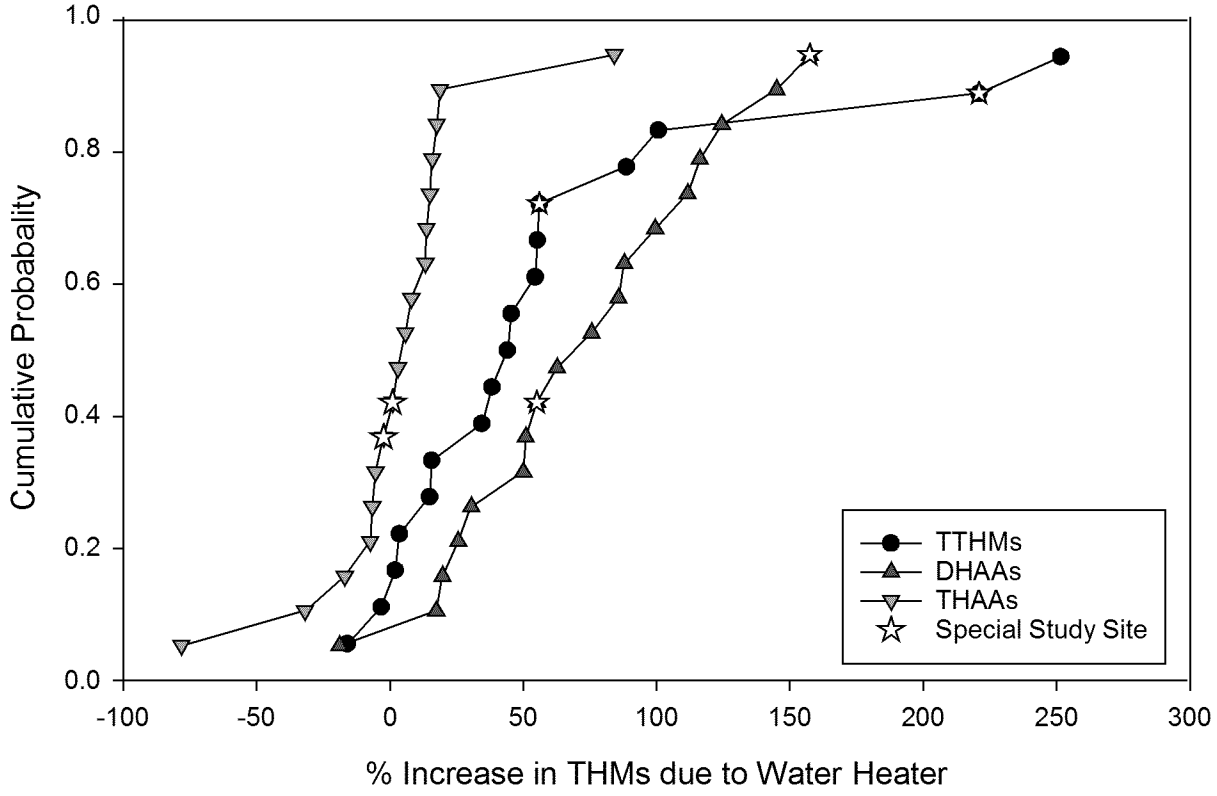

Figure 4. Increases in TTHM, Dihaloacetic Acid and Trihaloacetic Acid Concentrations between Hot and Cold water for US Homes with Tank Heaters (Reckhow, unpublished database). Stars are from two intensively monitored sites in a single system using free chlorine with low (upper star) and high (lower star) residence time.

Haloacetic Acids (HAAs)

The average cold water HAA5 concentration from the two Flint homes was 18.1 μg/L. This is close to the Grand Blanc control samples (19.7 μg/L). These HAA concentrations are near the national average (Figure 5), and that probably reflects a balance of temperatures and the high quality of the Detroit River – Lake Huron source. Long residence times in the Great Lakes system probably results in photodegradation and biodegradation of terrestrial precursors that contribute to HAA formation. Changes in concentration due to water heating in the Flint samples were small to moderate for the trihaloacetic acids (1% and 30% increase). In contrast, the dihaloacetic acids showed modest decreases (2% and 16% decrease). While not the typical pattern, these changes are within observations from the national database (Figure 4).

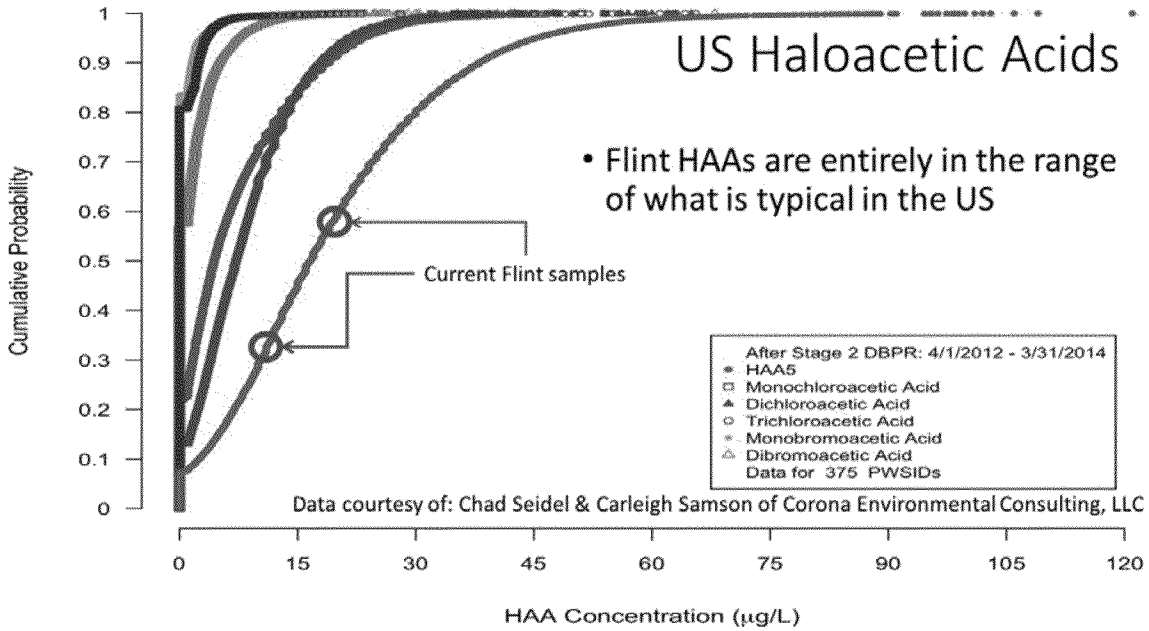

Figure 5. Comparison of Flint Distribution System HAA5s with National Database Prepared by Seidel and Samson.

Total Organic Halogen (TOX)

The Total Organic Halogen (TOX) group of methods includes Total Organic Chlorine (TOCl), Total Organic Bromine (TOBr), and Total Organic Iodine (TOI). This group of parameters is viewed as an estimate of the total amount of halogen atoms that are covalently bound to organic carbon. It is broken down into specific halogens: chloride, bromide and iodide. The TOBr and TOI are of special interest because of the tendency of brominated and iodinated organic compounds to test as more toxic than their chlorinated analogues. For reasons that are not clear, all of these data showed excessive breakthrough in the activated carbon adsorption step. Thus, they did not pass the QC criteria and the data will not be reported.

Haloacetonitriles (HANs)

The simplest and most prevalent group of halonitriles are the haloacetonitriles (HANs). As with many families of DBPs the HANs can be singly halogenated (Monohaloacetonitriles – MHANs)

doubly halogenated (Dihaloacetonitriles – DHANs) or triply halogenated (Trihaloacetonitriles – THANs). As a general rule Dihaloacetonitriles (DHANs), are found at higher levels of concentration than mono- and trihaloacetonitriles in drinking water. Also, because most systems have moderate to low bromide levels, the HANs that are most commonly seen are trichloroacetontrile (TCAN) and the three DHANs (DCAN, BCAN and DBAN). In the Flint samples, TCAN was below the MDL for all 8 samples and the DHAN species were similarly low (Table 4a). Figure 6 shows national occurrence data for DHAN graphed against the TTHM data from those same systems. The THMs are used as a benchmark recognizing that some drinking waters will have a lot of natural DBP precursor and therefore will tend to produce more DBPs of all kinds. Fortunately, Flint's water (from the Detroit system) has naturally low levels of THM precursors so that it the box representing those samples shows up toward the left side of figure 6. In addition, the level of DHANs in Flint water is similarly low, so the box is less than half was up the vertical scale. The green and red symbols in this figure come from the recent 11-city Water Research Foundation (WRF) study (Reckhow et al., 2016). The green symbols are from systems that used free chlorine, like Flint. In addition, the box and whisker symbols are from the EPA 12-city study (Weinberg et al., 2002). Finally, the large circle and cross represent averages from the 1997-99 information collection rule (ICR) as summarized by Blank et al., 2002.

Comparison of hot and cold data show substantial decreases for locations B and C and substantial increases for locations A and D. None of these data could be considered abnormal. Recent studies have shown that DHANs can increase at locations of low water age and if the water has only been in the water heater for a short time (Liu et al., 2014). Otherwise thermal degradation takes precedence and the DHAN values decrease markedly.

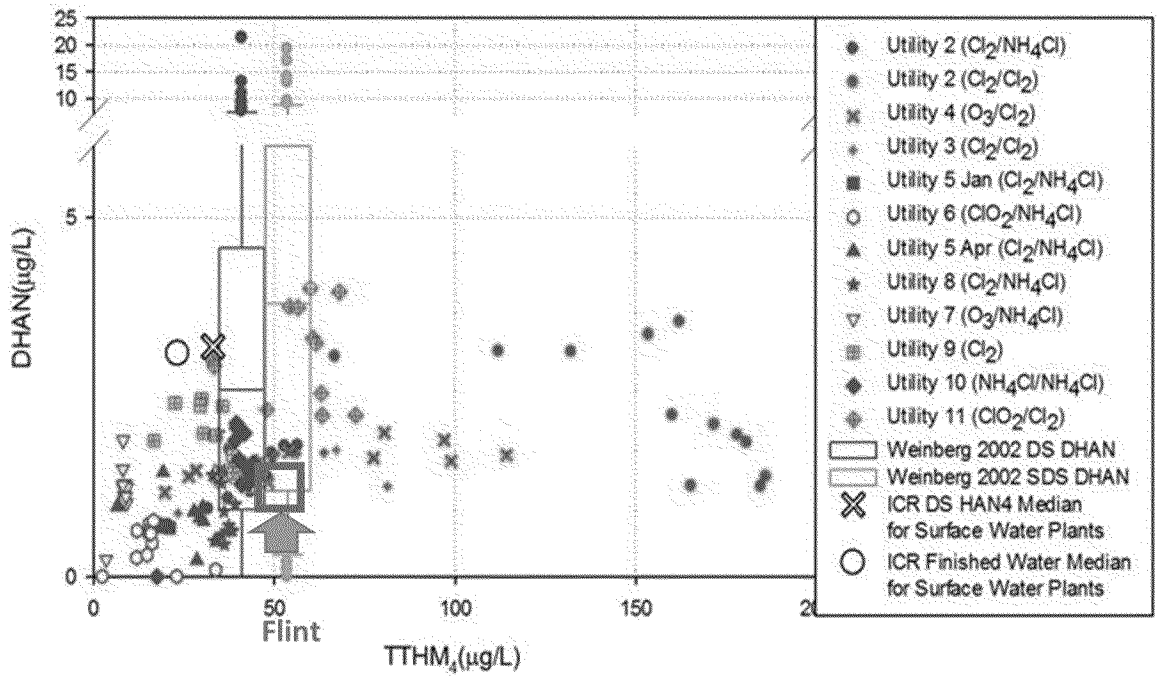

Figure 6. Dihaloacetonitrile concentrations compared to the corresponding TTHM concentration for the WRF and EPA surveys and the ICR

Haloketones (HKs)

The most commonly detected haloketone species are 1, 1-dichloropropanone and 1, 1, 1-trichloropropanone. Nationwide occurrence data (ICR) show median concentrations of 0.6 and 1.2 µg/L respectively for surface water treatment plants (Blank et al., 2002). Median values for DCP were found to be higher in chloramine systems, whereas median TCP concentrations were a bit higher in free chlorine systems. The values measured in Flint were quite low (Table 4a; Figures 7 and 8), especially for the TCP which tends to be elevated in free chlorine systems.

Heating is known to cause accelerated degradation of TCP (Liu et al., 2014). This loss of TCP in the hot water could not really be verified in these samples as the cold water values were so low. However, location D seem to show and increase in TCP which is not commonly seen elsewhere. This might be related to the rather unusually high chlorine residual in the hot tap at this location. In contrast DCP tends to increase in water heaters, and this increase is evident in locations A, B and D. Nevertheless, the final concentrations are still quite small compared to the national database.

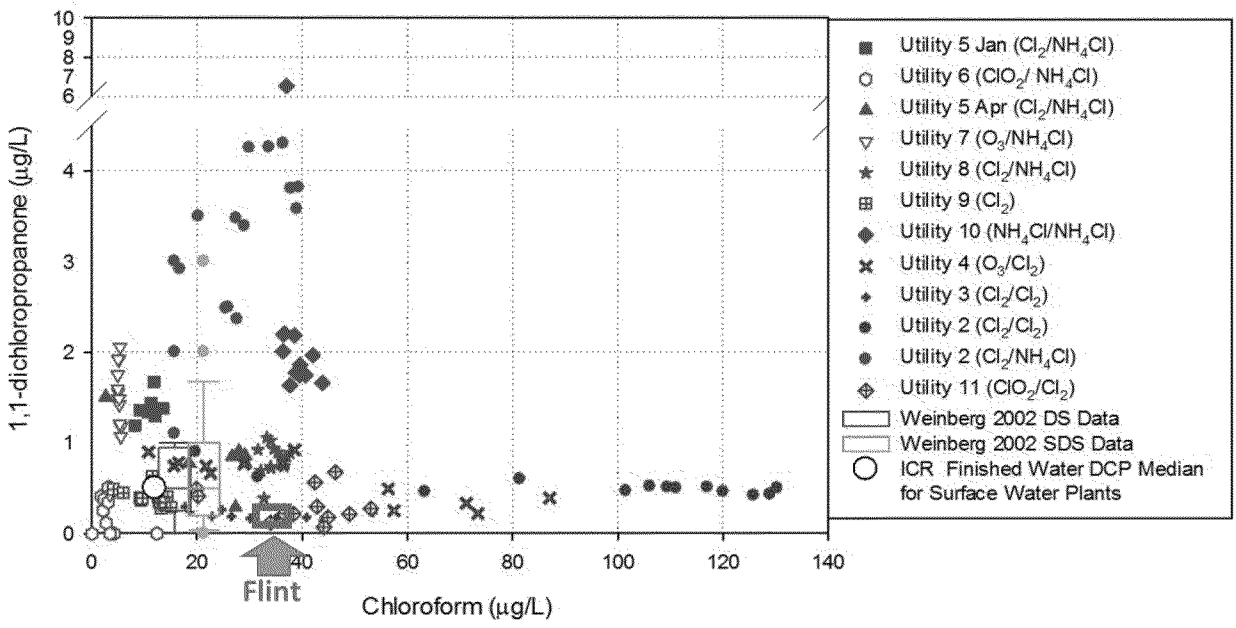

Figure 7. 1,1-Dichloropropanone concentrations vs the corresponding Chloroform concentrations: Flint samples compared to the National Database (the WRF and EPA surveys and the ICR)

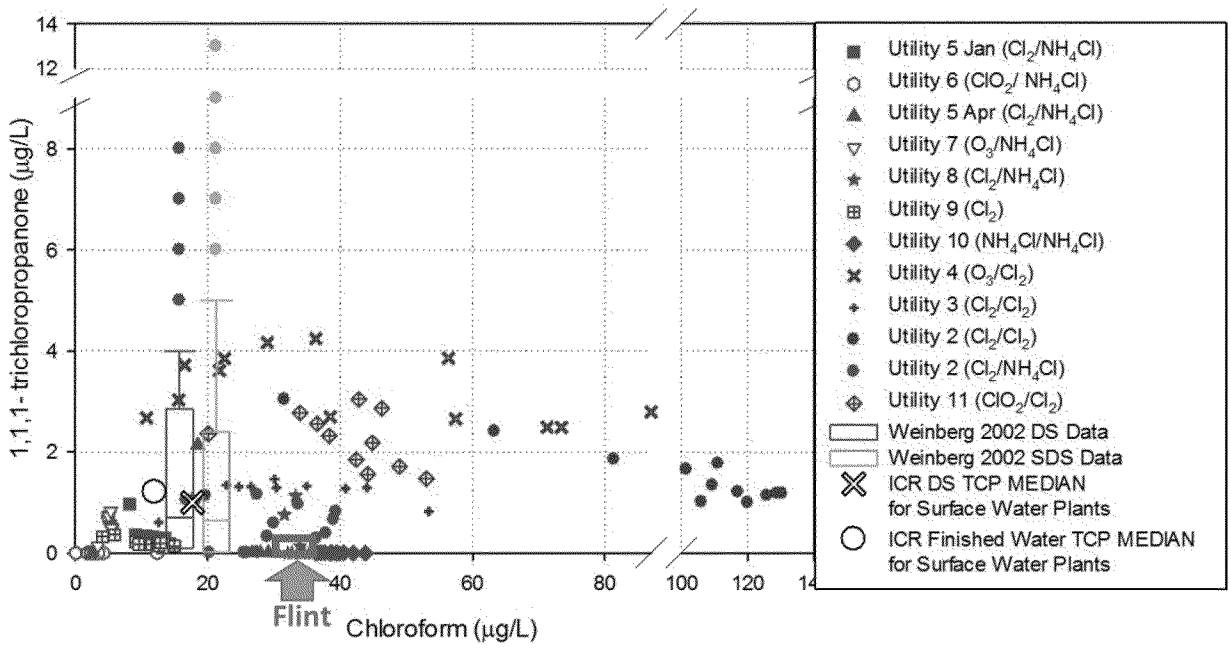

Figure 8. 1,1,1-Trichloropropanone concentrations vs the corresponding Chloroform concentrations: Flint samples compared to the National Database (the WRF and EPA surveys and the ICR)

Halonitromethanes (HNMs)

The Halonitromethanes (HNMs) is another group of unregulated disinfection by-products which have received much attention. Toxicological study conducted by Plewa et al. (2004) showed both cytotoxicity and genotoxicity of HNMs to be an order of magnitude higher than THMs and HAAs. In total, nine species are categorized as HNMs. They are bromonitromethane (BNM), dibromonitromethane (DBNM), tribromonitromethane (TBNM), chloronitromethane (CNM), dichloronitromethane (DCNM), trichloronitromethane (TCNM or CP [chloropicrin]), bromochloronitromethane (BCNM), dibromochloronitromethane (DBCNM), and dichlorobromonitromethane (DCBNM). Among these species, chloropicrin has been studied more than other species since it was first detected in late 1970s and analytical standard have been available for it since then. This compound is also the most prevalent of the group.

The HNMs are sometime associated with pre-oxidation with ozone or even UV light. As the Flint system uses neither, high levels of HNMs or chloropicrin are not expected. In fact, we see very low levels (Table 4a, Figure 9). The HNMs are one group of compounds that seem to increase substantially in tank water heaters. This is probably related to their high level of thermal stability. Increases from cold to hot is in fact what was observed in Flint (Table 5a), however the levels in the hot water are still quite low.

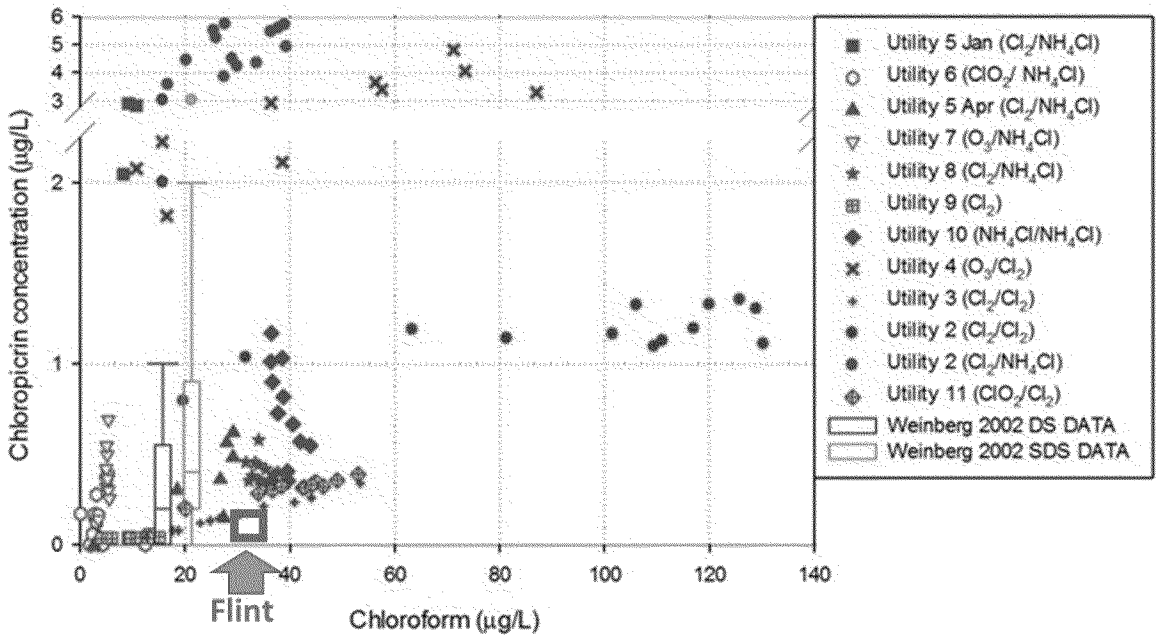

Figure 9. Chloropicrin concentrations vs the corresponding Chloroform concentrations: Flint samples compared to the National Database (the WRF and EPA surveys and the ICR)

Halobenzoquinones (HBQs)

These compounds were postulated by Bull et al (2006) to be likely byproducts and also possible bladder carcinogens. Subsequent work funded by the WaterRF led to an analytical method and the detection of HBQs in chlorinated drinking water (Zhao et al., 2010). For the past 3 years, UMass has been measuring HBQs in finished and distributed water (Mohan and Reckhow, 2016).

The concentrations found in Flint were typical of systems using free chlorine. Figure 10 shows where they appear on a cumulative distribution plot of systems sampled at UMass. While it looks like one of the Flint samples is at the high extreme, this is only an artifact of our sampling design which has favored chloramine systems. Like the regulated DBPs, formation of HBQs is considerably slower in the presence of combined chlorine. Dibromobenzoquinone (DBBQ) was not detected in any of the samples. Again this is typical for systems with low bromide as suggested by the distribution of THM species in these samples.

In, contrast, no HBQs were found in the hot water taps from Flint. This was not surprising. We know that these compounds undergo thermal degradation forming hydroxyl derivatives and other products. This seems to be happening in the hot water tanks from the residences we sampled in Flint.

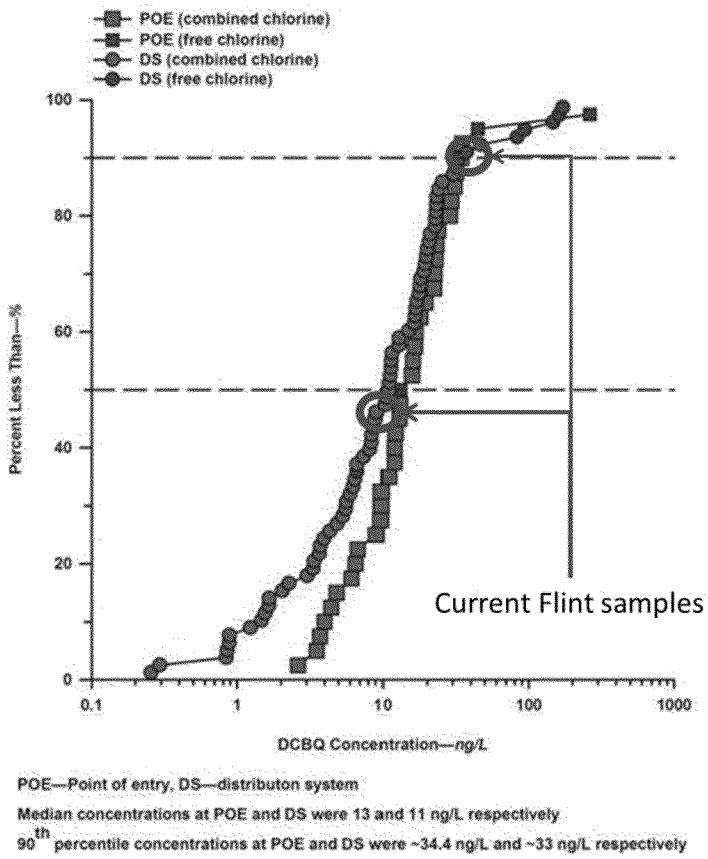

Figure 10. Dichlorobenzoquinone concentrations in Flint compared to existing database from Selected US Utilities (from: Mohan and Reckhow, 2016)

Haloacetamides (HAMs)

The Haloacetamides (HAMs) share many similarities with the HANs. In fact, HANs can readily degrade to form HAMs, and their organic precursors in natural waters are thought to be similar. Like the HANs, it is the trihalogenated species (especially trichloroacetamide or TCAM) and the three bromo-chloro dihalogenated species (DCAM, BCAM and DBAM) that are most prevalent. For this current sampling event, only the three dihaloacetamides (DHAMs) were found above the detection limit.

The DHAM concentrations are in the mid-range for those seen in other cities across the US (Table 4a, Figure 11). They may even be a bit higher than the average, but only slightly. Since Flint maintains a free chlorine residual, we propose that the HAMs in the cold water are mostly present as the N-chlorinated derivatives. This will be discussed a bit more in the next section.

The four sets of hot and cold water samples show little change due to passage through the hot water tank. This probably reflects the thermal stability of the HAMs, and more to the point, the N-chloro-HAMs.

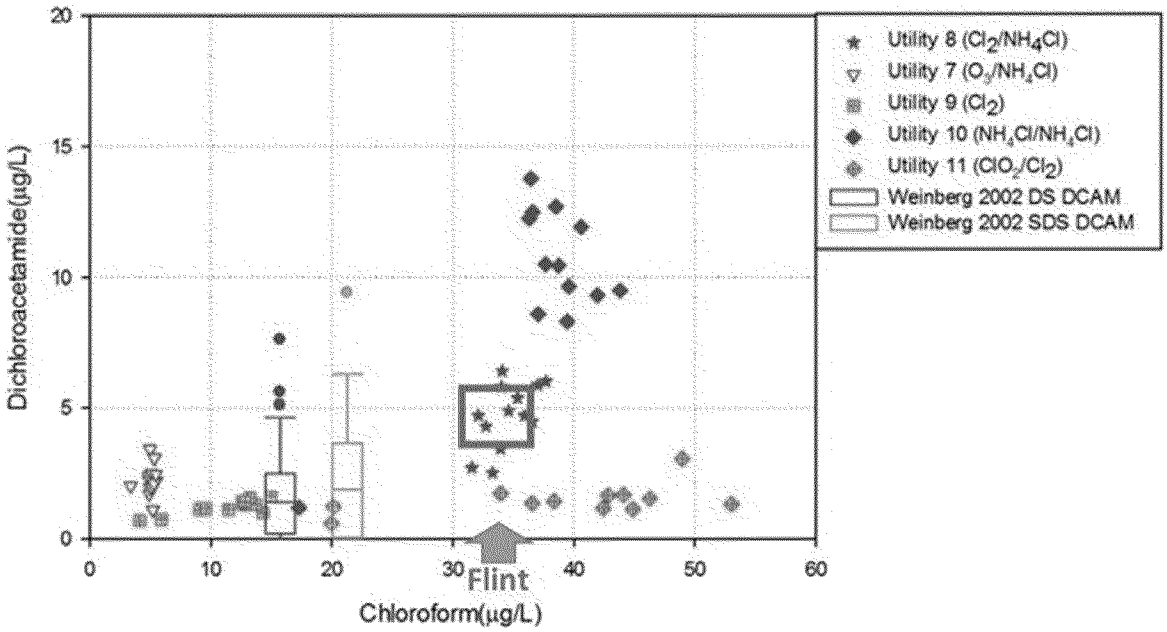

Figure 11. Dichloroacetamide concentrations vs the corresponding Chloroform concentrations: Flint samples compared to the National Database (the WRF and EPA surveys and the ICR)

N-Chloro-Haloacetamides (N-Cl HAMs)

These are a relatively new class of DBPs that can be formed by addition of chlorine to the nitrogen atom on HAMs. This reaction occurs very quickly in systems using free chlorine and the product is quite stable in most distribution systems (Yu, 2016). This group of compounds is of interest because they are members of the group of organic chloramines that have been proposed as having special concern regarding chronic disease (Bull et al., 2006).

An analytical method has very recently been developed for the N-Cl HAMs at UMass (Yu, 2016) and these data from Flint are among the very small pool of data that exists for this class of DBPs. We suspect that most of what has previously been identified as HAMs was actually N-Cl HAMs that had been chemically reduced to HAMs by addition of preservatives. Therefore, the most appropriate dataset to place these values into context is the one on HAMs (e.g., Figure 11).

With the exception of one of the reference locations (C) all N-Cl-DCAM concentrations were similar to the corresponding DCAM values. In contrast, the N-Cl-BCAM concentrations are substantially higher than the BCAM values. This is surprising based on our understanding of this system, but there are so little data on these compounds we cannot say if this is unusual.

The conclusion for the N-Cl HAMs is essentially the same as for the HAMs. We suspect that the concentrations are in the mid-to-high range based on national occurrence data. Furthermore, these compounds seem to persist in hot water, but not at elevated levels.

Aldehydes (ALDs)

The small alkyl mono- and di-aldehydes are common oxidation products of natural organic matter. While they are often associated with the use of ozone, all oxidants and disinfectants will produce some level of aldehyde byproducts.

The concentrations from the Flint samples were all in the low µg/L range which is typical of systems using free chlorine. Unfortunately, there is not a good national dataset for aldehydes in US plants. The Information Collection Rule dataset only covered 41 plants that used either ozone or chlorine dioxide (Blank et al., 2002). Detection limits were high for this work (5 µg/L) and as a result most samples were reported as BDL. Nevertheless, the 50%ile for formaldehyde and the 90%ile for Glyoxal were slightly above the 5µg/L detection limit. The concentrations in the Flint cold water samples were all below this level (Table 4b).

Heating and passage through water heaters seemed to substantially elevate the levels of the aldehydes in most cases (Table 5b). Very little data exist on the impacts of home tank water heaters on aldehydes. Nevertheless, it's not surprising that these thermally stable compounds would persist and even continue to form under the conditions in a home water heater. None of the concentrations measured exceeded 6 µg/L.

SECTION D: GENERAL CONCLUSIONS

The following conclusions are based on the suite of DBPs that were measured by UMass from samples collected on May 31, 2016.

The two cold water samples collected from Flint homes were typical of what exists around the US especially when comparing systems that use free chlorine as a residual disinfectant. Some DBPs were near or even below the national average, and some were slightly above average. In general, the two Flint samples had DBP concentrations that were comparable to that of the control community (Grand Blanc).

Samples collected from the hot water taps showed changes, with some DBPs decreasing in concentration and some increasing. The changes that were noted are typical of what we've seen from other systems or from what we expect based on the known thermal stability of the particular DBP compounds.

In summary, we didn't see anything unusual or alarming in the Flint water samples from these two locations.

SECTION E: REFERENCES

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